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CONTENTS

ILLUSTRATIONS

TABLES

UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	kg	kilogram
cm^3/g	cubic centimeter per gram	L	liter
g	gram	min	minute
g/L	gram per liter	mL	milliliter
h	hour	mL/min	milliliter per minute
in	inch	pct	percent
in Hg	inch of mercury (atmospheric pressure)	ppm	part per million

Na_2CrO_4 FROM DOMESTIC CHROMITE CONCENTRATES BY AN ALKALI-FUSION METHOD

By Gary L. Hundley,[1] R. E. Mussler,[2] R. A. Holmes,[3] and R. S. Olsen[4]

ABSTRACT

The Bureau of Mines has devised a procedure to recover chromium chemicals from concentrates derived from low-grade domestic chromites. These domestic chromites contain silicon and aluminum impurities at levels that are too high to permit processing by present industrial processes. The Bureau procedure consists of reacting chromite with molten NaOH under oxidizing conditions to form sodium chromate (Na_2CrO_4). The reaction product is leached with methanol to recover the majority of the unreacted NaOH, then with water to extract the Na_2CrO_4 and the remainder of the NaOH. The Na_2CrO_4 product is recovered by evaporative crystallization from the aqueous solution.

This report presents laboratory results of studies to determine the optimum leaching conditions for the reaction products of several domestic chromite concentrates. Results of solution purification and crystallization studies are also presented. The concentrates are from a variety of sources including the Stillwater Complex in Montana, Red Bluff Bay and the Kenai Peninsula in Alaska, and a Ni-Co laterite from southern Oregon. Sodium chromate crystals were produced that contained less than 0.01 pct NaOH.

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INTRODUCTION

Chromium is a commodity that is essential to the Nation's metallurgical, chemical, and refractory industries. The United States has no domestic production or economic reserves of chromite, the only commercial ore of chromium, and must rely on imports to meet national needs. The chemical industry consumes approximately 25 pct of the chromite for the production of pigments, chromic acid for electro plating, and other chemicals used for leather tanning, wood preservatives, catalysts, and corrosion inhibitors (1).[5]

Commercial processes presently used to chemically treat chromite concentrates include an oxidizing roast of the chromite with Na_2CO_3 and CaO in a rotary kiln at temperatures around 1,100° to 1,150° C. The amounts of reagents and a diluent are controlled so that the reaction mixture remains as a solid phase in the kiln (2). Concentrates produced from domestic chromite deposits contain too much silicon to be processed by this method. The silicon forms molten, sticky reaction products with the Na_2CO_3, which cause balls or rings of material to form in the kiln, hindering its operation. The aluminum content in domestic resources also is high, resulting in an excess consumption of reagents (3).

A simplified flowsheet for the Bureau of Mines procedure to recover chromium chemicals from domestic chromite concentrates is shown in figure 1. Briefly, the procedure consists of reacting the chromite at 550° to 650° C with an excess of molten NaOH under oxidizing conditions to produce Na_2CrO_4. The product from the fusion reaction is solidified, crushed, and leached with methanol in a countercurrent procedure. The methanol leach removes the majority of the excess NaOH while only removing a trace of the Na_2CrO_4. This separation can be accomplished because of the large difference in solubility of the two compounds in methanol. For example, the solubility of Na_2CrO_4 in a methanol solution containing 10 pct NaOH is only 0.013 pct (4). The methanol solution is then evaporated to recover the NaOH, which is recycled to the fusion reactor.

The residue from the methanol leach is water leached to recover the remainder of the NaOH and the Na_2CrO_4. Silicon and aluminum compounds are removed from the aqueous solution by adding a soluble silica compound to adjust the Si-Al ratio so the compound, $NaAlSiO_4$, will form and precipitate from solution. The final Na_2CrO_4 product is recovered from the aqueous solution by evaporative crystallization. The mother liquor exiting the crystallizer is evaporated, and the solids are recycled to the fusion reactor. The Na_2CrO_4 product from this procedure is a basic industrial chemical and can be used to produce the other common Cr compounds in commercial use.

This report describes experimental results for the leaching, solution purification, and crystallization steps of the procedure. A previous report (5) describes the experimental results of the fusion step for a variety of concentrates. The general equation for the fusion reaction of the chromite with the NaOH is

$$FeO \cdot Cr_2O_3 + 4NaOH + 7/4\ O_2 \rightarrow 2Na_2CrO_4 + 1/2\ Fe_2O_3 + 2H_2O. \quad (1)$$

Previous work by Chandra (6) showed that an excess of NaOH must be used to maintain a fluid reaction mixture. A NaOH-to-chromite weight ratio of ~4:1 (22.4:1 mole ratio) typically is necessary to maintain fluidity and to obtain good conversion of the chromium in the chromite to Na_2CrO_4. Reaction products build up on the surface of the chromite particles preventing further reaction so the mixture must be kept well agitated to remove these surface products. A stirred-pot-type reactor was used in the present work. Studies also are being conducted in Japan on a similar procedure using sodium nitrate as the oxidizing medium rather than air as used in the

[5]Underlined numbers in parentheses refer to items in the list of references at the end of this report.

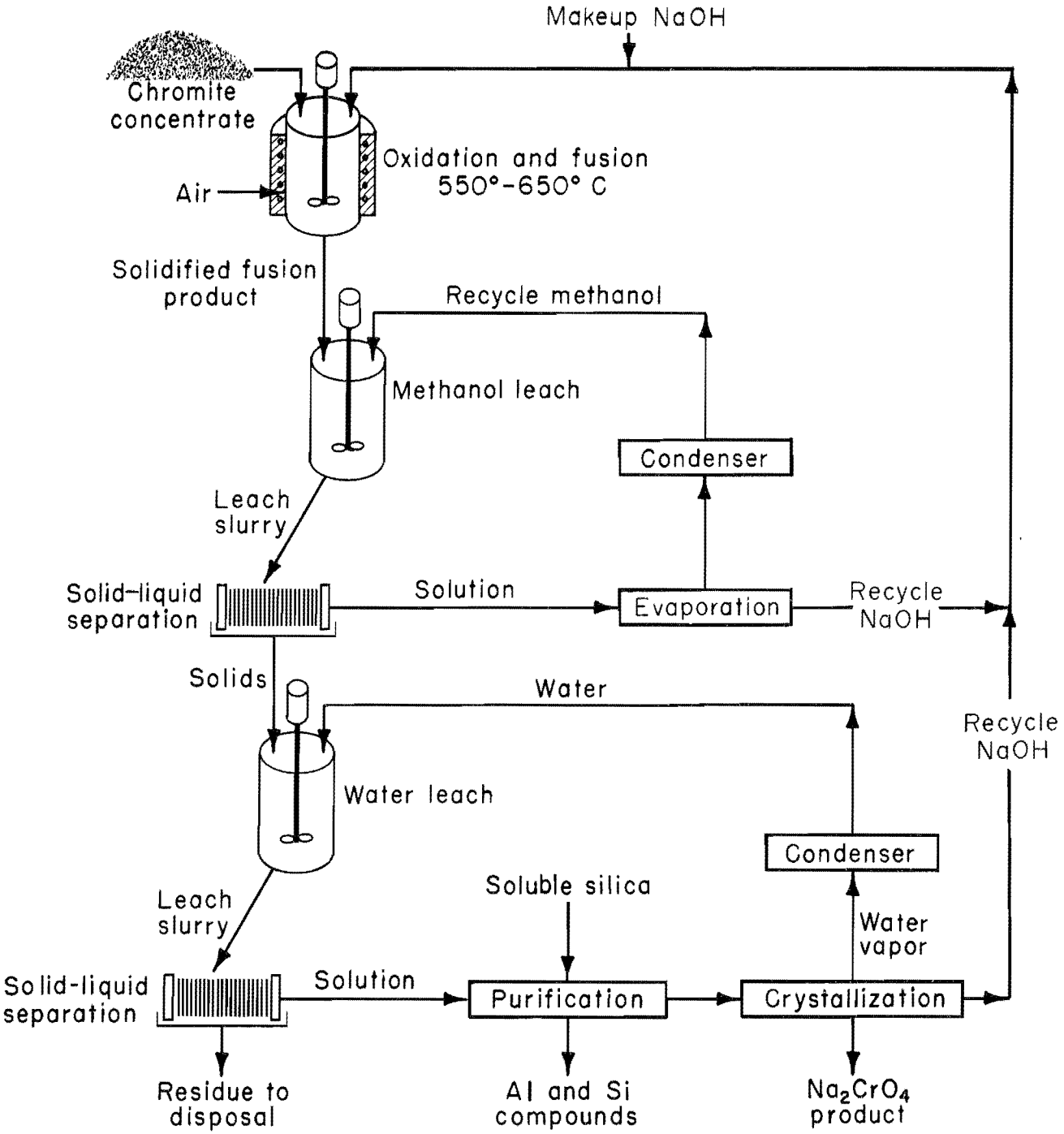

FIGURE 1.–Chemical processing of chromite.

Bureau method (7-8). The results of the Bureau study indicated that chromium conversions in the fusion reactor as high as 98.9 pct can be obtained for high-chromium, high-grade concentrates. For marginal high-iron concentrates, the chromium conversions were in the 90- to 94-pct range, and with submarginal chromites the chromium conversion was in the 68- to 81-pct range.

RAW MATERIALS

The chromite concentrates tested in this study and presented in a previous Bureau report (5) were obtained from a variety of sources in Alaska, California, Montana, and Oregon. They were categorized in one of the following groups:

1. High chromium (metallurgical-grade) chromite that contained a minimum of 46 pct Cr_2O_3 with a Cr-Fe ratio >2.0:1.

2. High-iron (chemical-grade) chromite that contained 40 to 46 pct Cr_2O_3 with a Cr-Fe ratio of 1.5 to 2.0:1.

3. Marginal chromite that met either the grade or Cr-Fe ratio requirements for one of the classifications above and very nearly met the other.

These classifications were obtained from Dahlin (9-10). The four concentrates tested in the leaching and solution purification steps are listed in table 1 with their origin, composition, Cr-Fe ratio, and quality classification. Ten additional samples were tested, with results reported previously (5).

Test results for two concentrates from Alaska are reported in this paper. One sample, from Red Mountain, was a high-chromium concentrate containing 56.4 pct Cr_2O_3 and 1.4 pct SiO_2 with a Cr-Fe ratio of 2.8. The other sample was a high-iron concentrate from Red Bluff Bay containing 41.7 pct Cr_2O_3 and 8.0 pct SiO_2 with a Cr-Fe ratio of 2.0.

A concentrate from southern Oregon was derived from a Ni-Co laterite leach residue. This material was the residue remaining after processing in the Bureau's roast-leach procedure for recovering nickel and cobalt. Beneficiation of this residue resulted in a high-iron chromite concentrate containing 41.5 pct Cr_2O_3 and 1.7 pct SiO_2 with a Cr-Fe ratio of 1.8 (11).

A concentrate from the Mouat Mine in the Stillwater complex in Montana also was tested. This was a marginal, high-iron material having a Cr-Fe ratio of 1.5 and a high silicon content of 8.5 pct SiO_2.

The impurity content of the chromites is generally of two types: either gangue components associated with the chromite grains or lattice impurities in the chromite mineral itself. The silicon impurity is generally in the form of silicate minerals such as olivine (Fe-Mg silicate) and serpentine (magnesium silicate). Silicon is not present in significant quantities in the form of silica minerals such as quartz.

The chromite mineral is a spinel structure theoretically represented by the formula $FeO \cdot Cr_2O_3$. Magnesium can substitute for the Fe^{2+}, and Al^{3+} and Fe^{3+} can substitute for the Cr^{3+} in the crystal lattice, giving the formula $(Mg,Fe)O \cdot (Al,Fe,Cr)_2O_3$. In addition to the lattice impurities, additional iron in the form of magnetite (Fe_3O_4) is commonly associated with the chromite grains.

TABLE 1. - Head analyses of chromite concentrates, percent

Sample	Cr_2O_3	Fe	MgO	Al_2O_3	SiO_2	Cr-Fe ratio	Quality
Alaska:							
Red Mountain (Kenai Peninsula)...	56.4	13.7	15.2	8.8	1.4	2.8	High-Cr.
Red Bluff Bay (Baronof Island)...	41.7	14.3	16.9	9.2	8.0	2.0	High-Fe.
Southern Oregon: Eight Dollar Mountain laterite.....	41.5	16.1	12.4	22.3	1.7	1.8	Do.
Montana: Mouat (Stillwater complex).....	36.1	16.7	16.3	15.0	8.5	1.5	Marginal.

COUNTERCURRENT LEACHING

EQUIPMENT AND PROCEDURES

The solidified fusion product from the first step of the process (fig. 1) was crushed and ground to minus 20 mesh. All grinding and screening operations were performed in a dry box to prevent the absorption of moisture by the material. Single-stage batch leach tests were conducted on this material to determine the appropriate conditions to use in countercurrent leach tests. These showed that the solid-to-liquid ratio and the amount of water in the methanol were important factors. In particular, the water in the methanol solvent had to be limited to 5 pct or less to prevent solubilization of Na_2CrO_4.

Countercurrent leach tests were performed in a stepwise manner using the Shanks system to simulate steady-state conditions (12). Each leach stage was performed in a 250-mL sample bottle using a small, three-bladed propeller for mixing. The solid-liquid separation step, after leaching, was conducted by centrifuging the sample in bottles. The liquid was decanted and added to the next appropriate stage. The solids in their same bottle were advanced to the next leaching stage. In this manner, the solids remained in the same bottle for all three leach stages and did not have to be removed, minimizing handling losses.

Fusion products from the four concentrates reported in the Raw Materials section were leached in three countercurrent stages with methanol, then the residue from the methanol leach was leached with water in three countercurrent stages (fig. 2) in the equipment previously

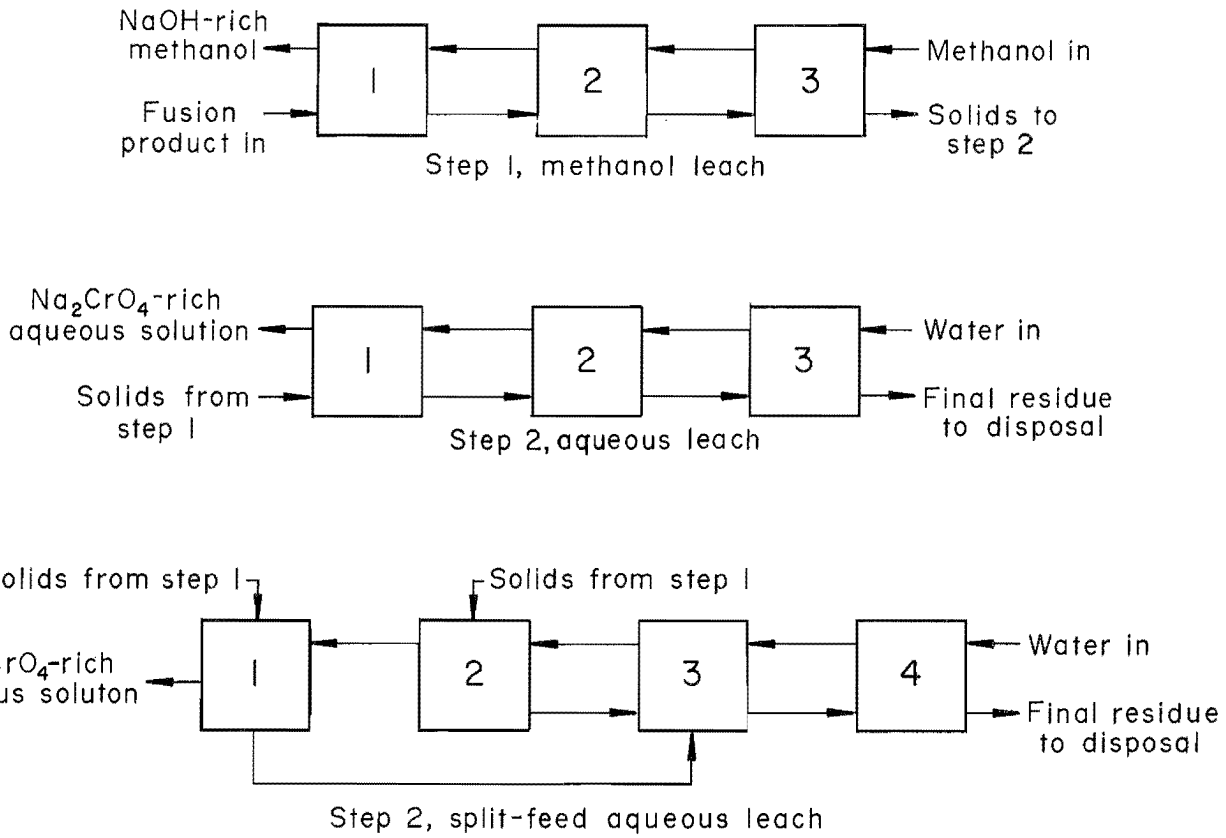

FIGURE 2.--Countercurrent leach flowsheet.

described. All the leach tests except one were conducted with 30 pct solids in the leach slurry; the other test was conducted at 15 pct solids. The 30-pct-solids value was chosen in order to produce methanol leach solutions that were nearly saturated with NaOH, while the 15-pct-solids value was chosen to determine if a greater NaOH extraction could be obtained with a more dilute solution. This information is necessary to select the procedures that will minimize the energy required to evaporate the methanol so that the NaOH can be recycled. Leach time was 30 min in the methanol leach step and 10 min in the water leach. A particle size of minus 20 plus 32 mesh was used in most of the tests in the methanol leach. The particles resulting from the methanol leach was used in the water leach, and these particles were quite fine because the original particles were broken down as the methanol removed the NaOH. A methanol solvent with a concentration of 95 wt pct methanol and 5 pct water was used in all tests.

RESULTS AND DISCUSSION

The results indicate that three-stage countercurrent methanol leaching removed 84 to 94 pct of the unreacted NaOH. The higher extraction was obtained from fusion products containing a higher ratio of NaOH to chromite. Testing showed that only 1 pct more NaOH would be removed with a fourth stage. As shown in table 2, only a trace of the chromium was found in the methanol solution. The aqueous solution contained the remainder of the NaOH and 90 to 99 pct of the soluble chromium. The remainder of the chromium and trace amounts (<0.4 pct) of NaOH were detected in all residues from the water leach except for the Red Bluff residue. The soluble chromium remaining in the leach residue from all four materials represents inadequate washing of the residue. This material could be readily removed by the addition of one or two more aqueous leach stages. Additional aqueous stages were not used in the test program because the number of cyles to reach equilibrium was increased greatly and also required the use of much more material. Five complete leach cycles were used for both the methanol and aqueous leach steps to attain equilibrium conditions.

The NaOH concentration in the methanol solution ranged from 146 g/L for the Red Mountain fusion product to 224 g/L for the Mouat material. A saturated NaOH solution in methanol contains approximately 240 g/L NaOH. The Na_2CrO_4 concentration in the aqueous solution was in the range of 249 to 280 g/L, and the NaOH was 35 to 80 g/L. An aqueous saturated solution at 25° C would contain approximately 530 g/L Na_2CrO_4 and 150 g/L NaOH.

The chromium concentration in the aqueous solution was relatively dilute compared with the mother liquor concentration that would be used in a crystallizer in the product recovery step of the process. This requires that a large volume of water be evaporated in the crystallizer, with its corresponding high energy consumption. The solution concentration cannot be increased much by increasing the percent of solids in the leach slurry because the mixture would contain too many solids to mix effectively. To produce a more concentrated solution, a split-feed arrangement (shown in

TABLE 2. - Results of two-step, three-stage countercurrent leach tests, percent

Concentrate	NaOH-chromite wt ratio in fusion	Solids in leach	Extraction				Residue	
			Methanol		Water		NaOH	Cr
			NaOH	Cr	NaOH	Cr		
Red Mountain.....	2:1	30	88.8	Tr	11.1	98.7	0.1	1.2
Red Bluff Bay.....	4:1	30	87.9	Tr	7.7	96.5	4.4	3.5
Eight Dollar Mountain...	4:1	30	84.0	Tr	15.6	96.8	.4	3.2
Mouat.....	6:1	30	94.3	Tr	5.5	90.0	.2	10.0
	6:1	15	92.7	Tr	7.2	98.6	.1	.4

Tr Trace.

figure 2) was tested. In this procedure, fresh feed equivalent to 30 pct solids was fed into each of the first two leach stages. The residues from each of these stages was combined in stage 3. Enough soluble material was removed from the solids in each of the first two stages so that when the solid residue from each of these stages was combined, the resulting slurry contained about 30 pct solids. Four stages were used in this test. This was not enough because the final residue contained an appreciable amount of soluble chromium and NaOH. The final leach solution from this procedure contained 449 g/L Na_2CrO_4 and 185 g/L NaOH. The final residue contained 12.1 pct of the soluble chromium fed to the leach circuit and 14.1 pct of the soluble NaOH. The leaching sequence was repeated for seven cycles to produce the final equilibrium conditions. The separation of solids from liquids in this procedure was very difficult, especially in the first stages with the concentrated solutions. The solutions were very viscous, and the particle size was small, making for a difficult separation. A more reasonable procedure would be to operate the first two leach stages at 20 to 25 pct solids to allow an easier solid-liquid separation while still producing solutions more concentrated than those obtained with a straight countercurrent leach at 30 pct solids. At least two additional stages would also be required to insure that all the soluble chromium and NaOH were removed from the residue.

SOLUTION PURIFICATION

No significant amounts of impurities were found in the methanol solution. Aluminum and silicon were found in the 10- to 50-ppm range.

The major impurities that were solubilized in the aqueous solution by the fusion reaction were silicon and aluminum. A minor amount of ferrous iron (Fe^{2+}) also was soluble, but it oxidized on exposure to air and precipitated from solution. Magnesium was a major impurity in the chromite concentrates but did not become soluble to any extent. Solution concentrations were typically 1 ppm Mg or less. The aluminum extraction tended to follow the same trend as the chromium extraction. This would be expected because the aluminum substitutes for chromium in the chromite lattice. As the chromium was reacted, the aluminum also would be exposed and react with the NaOH.

The silicon extraction appeared to be more random, although it generally decreased with time after increasing for the first hour of the reaction. Reactions at 550° C often resulted in greater extractions than those at 650° C. These lower extractions at the longer reaction times and higher temperature may be due to the formation of high molecular weight, insoluble metal silicates. Increasing the NaOH-to-chromite ratio in the fusion reaction generally resulted in an increased silicon extraction.

The total amount of silicon found in the aqueous solution after countercurrent leaching ranged from 1.6 to 13 pct of the total silicon content in the chromite. The aluminum content in the solutions ranged from 32 to 71 pct of the total amount in the chromite.

Dilute solutions such as those obtained from a single-stage leach can be purified of silicon and aluminum compounds by sparging CO_2 into the solution to reduce the pH so that silicon and aluminum compounds precipitate. This procedure is not effective with the stronger solutions produced by countercurrent leaching. Even after 90 pct of the unreacted NaOH in the methanol solution was removed, the aqueous solution still contained too much NaOH to reduce the pH by sparging. So much Na_2CO_3 was produced that the entire solution solidified as the Na_2CO_3 solubility was exceeded.

A procedure patented by Holtz (13) was used to purify solutions resulting from countercurrent leaching tests. In this procedure, a soluble silica compound was added to the solution so that the ratio of silicon to aluminum was adjusted to form the compound $NaAlSiO_4$, which then precipitated from solution. The silica compound was added in the form of

waterglass (Na_2SiO_3) or Ludox[6] suspension of colloidal silica. The solution was initially heated to 70° to 90° C for 30 min to 2 h after the silica compound was added, then the solution was boiled for 30 min to 1 h. In some cases, a crystallization seed in the form of sodalite ($NaAlSiO_4$) was also added to promote the formation of a more crystalline product. Other variables investigated were (1) solution temperature when the soluble silica compound was added, (2) temperature of initial heating step, (3) time at initial heating step, and (4) time at boiling temperature. These tests are summarized in table 3.

When the silica compound was added to the solutions, a thick gel initially formed, particularly in the case of the Ludox colloidal silica. The gel eventually broke down, but the best results were obtained when the silica was added slowly and a crystallization seed was used. The waterglass with a crystallization seed appeared to result in a better aluminum extraction, and the precipitate was easier to filter than when using the Ludox colloidal silica. This colloidal silica alone (i.e., without a crystallization seed) resulted in a gelatinous precipitate that was very difficult to filter. Boiling for a longer period of time also resulted in improved aluminum extractions and improved filterability. The amount of crystallization seed was based on the aluminum content of the solution and was calculated to be approximately 10 pct of the expected weight of the precipitate.

The precipitate obtained in these studies was identified by X-ray diffraction as $1.01Na_2O \cdot Al_2O_3 \cdot 1.68SiO_2 \cdot 1.73H_2O$. The chromium content of the precipitate ranged from 0.24 to 1.70 pct, with most of the values in the 0.7 to 0.9 pct range. Final aluminum content in the solutions was in the 0.3 to 0.9 g/L range, with the silicon content at 0.1 to 0.6 g/L.

[6]Reference to specific products does not imply endorsement by the Bureau of Mines.

TABLE 3. - Results of solution purification tests

Solution and soluble silica type	Addition temp[1]	Crystallization seed	Preheat temp, °C	Preheat time, h	Boiling time, h	Al extraction, pct	Si extraction,[2] pct
LATERITE							
Ludox.....	Hot.....	Yes.....	70-80	1	0.5	100	98.8
Do.....	...do...	No.....	70-90	.5	.5	99.8	97.8
Waterglass...	...do...	No.....	70-80	1	.5	94.5	99.9
Ludox.....	Cold....	Yes.....	70-80	1	.5	92.9	97.3
Do.....	Hot.....	Yes.....	70-80	1	.5	95.1	96.6
Waterglass...	Cold....	Yes.....	70-80	1	.5	96.0	97.0
Do.....	Hot.....	Yes.....	70-80	1	.5	96.5	96.8
Ludox.....	...do...	Yes.....	80-90	2	.5	96.7	96.2
Waterglass...	...do...	Yes.....	80-90	2	.5	94.9	97.0
RED MOUNTAIN							
Ludox.....	Cold....	No.....	70-80	1	0.5	43.3	98.0
Do.....	...do...	Yes.....	70-80	1	.5	59.6	98.3
Waterglass...	...do...	No.....	70-80	1	.5	84.4	95.8
Do.....	...do...	Yes.....	70-80	1	.5	87.8	99.1
Ludox.....	Hot.....	Yes.....	80-90	1	1	97.2	99.2
Waterglass...	...do...	Yes.....	80-90	1	1	97.5	99.2

[1]Cold--treated solution at ambient temperature.
Hot--treated solution at preheat temperature.

[2]Si extraction includes amount in original solution plus amount added to precipitate aluminum.

CRYSTALLIZATION

EQUIPMENT AND PROCEDURES

A semicontinuous vacuum evaporative crystallizer (fig. 3) was constructed of standard taper-joint glassware. The crystallizer body was constructed from a 3-L round-bottom flask that was heated with an electric heating mantle. A ground-glass shaft sealed with a mineral oil gland was used to stir the contents of the reactor. A vacuum was obtained in the system with a water aspirator, and the desired vacuum level was maintained with a pressure-relief valve. The condensate was collected in 500-mL flasks that were kept in an ice bath to prevent excessive loss of condensate due to the vacuum in the system. Fresh feed was added to the system at a known rate with a piston-type metering pump. Product crystals and mother liquor samples were obtained by means of a dip-tube placed in the crystallizer slurry. This tube was sealed to a hot-water-jacketed filter, and samples were obtained by releasing the system vacuum and applying a vacuum to the filter flask. Crystals were collected on the filter and a mother liquor sample was obtained from the filter flask.

In the general operation of the crystallizer, approximately 2 L of mother liquor of the desired composition was added to the crystallizer. Synthetic solutions were used for the mother liquor and feed solution rather than solutions produced from actual chromite concentrates during most of the testing. Synthetic solutions were used because of the lack of personnel and equipment to produce large quantities of actual leach solution. The solution was then heated to the desired temperature, and the vacuum was adjusted to induce boiling at this temperature. The temperatures generally used were 65° C or 80° to 85° C. Limited testing was done at 65° C because the necessary vacuum could not be maintained to induce boiling with the more concentrated solutions. After crystals began to form, the feed was started. The feed composition was kept constant at 40 g/L NaOH and 260 g/L Na_2CrO_4 for all the testing. A fixed feed rate of 10 mL/min was used in all tests. Every 30 min samples of the mother liquor and crystals were taken and the condensate flask was changed and the volume recorded. The weight of crystals and volume of mother liquor taken were determined by a

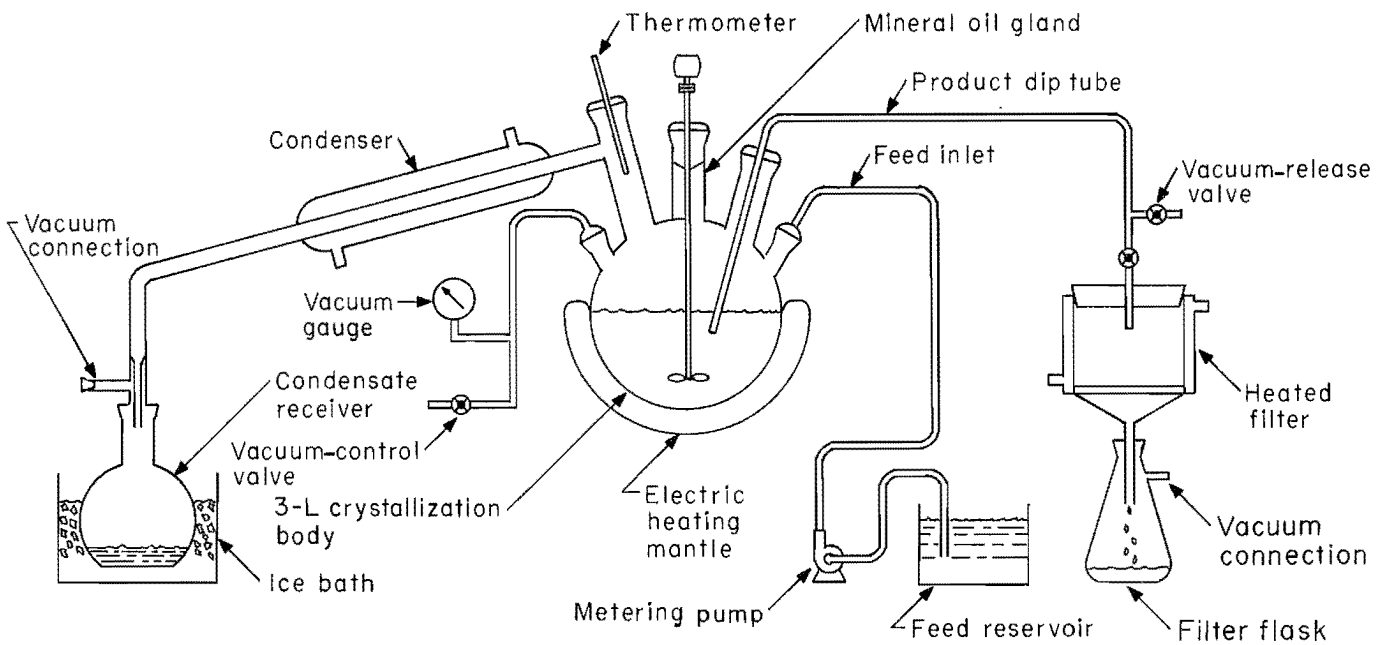

FIGURE 3.--Vacuum evaporative crystallizer.

material balance so that the concentration of NaOH and Na_2CrO_4 in mother liquor and the volume of mother liquor in the crystallizer remained unchanged. The rate of heat input to the crystallizer also was adjusted slightly to maintain steady-state conditions. As samples of mother liquor were obtained during the run, they were titrated for NaOH and Na_2CrO_4 concentration to insure that steady-state conditions were maintained.

The product crystals collected on the filter were washed with methanol to remove residual mother liquor adhering to the crystals. The volume of methanol was normally 2 cm^3/g of crystals. The methanol was applied in three portions and mixed with the crystals with each application. The resulting slurry was then vacuum filtered. Approximately 75 g of crystals was obtained with each sample. Removal of only 25 to 30 mL of mother liquor normally was required to maintain steady-state conditions in the crystallizer, but to obtain the necessary weight of crystals, approximately 250 mL of mother liquor had to be processed through the filter. A sample of mother liquor was taken from the filter flask, and the remainder was returned to the crystallizer. The crystals were dried in a drying oven and then kept in air-tight sample bottles while awaiting chemical analysis and a screen analysis.

RESULTS AND DISCUSSION

Synthetic Leach Solutions

The NaOH concentration in the mother liquor was varied from 422 g/L to 1,058 g/L. The corresponding saturated concentration of Na_2CrO_4 ranged from 330 to 93 g/L at these NaOH levels. As shown in table 4, the average crystal size ranged from 28 to 100 mesh, and the NaOH content in the crystals was generally less than 0.01 pct. The particle size shown is the average of all samples taken and represents the size for 50 pct of the weight. Higher levels of NaOH in the crystals are due to inadequate washing of the crystals and not to NaOH cocrystallized in the Na_2CrO_4 matrix. As the mother liquor became more concentrated, it became more difficult to wash the crystals. The maximum practical limit for the mother liquor composition was

TABLE 4. - Results of vacuum crystallization tests on synthetic solutions

Av mother liquor composition, g/L		Vacuum, in Hg	Temp, °C	Av crystal size, mesh	NaOH content in crystals, pct
NaOH	Na_2CrO_4				
422	330	27	74	28	<0.01
436	336	26	78	60	<.01
535	288	22	100	28	<.01
547	241	26	88	42	.01
564	223	26	84	(1)	<.01
604	205	27	84	42	<.01
654	192	27	85	48	<.01
655	221	27	88	60	<.01
676	188	27	88	42	<.01
680	194	27	80	60	<.01
685	202	27	87	65	<.01
686	192	27	85	42	.01
742	170	27	90	65	.05
775	178	27	93	48	.13
802	176	27	95	48	.01
886	191	27	105	100	.02
1,058	93	27	110	(2)	NAp

NAp Not applicable.
[1]Saturated Na_2CrO_4 aqueous solution used for wash; crystals fused together.
[2]Crystals too fine to wash.

around 800 g/L NaOH. As this level was exceeded, the solution became very viscous, and the particle size became very small, making washing difficult. The very small crystals also are not desired.

An attempt was made to correlate crystal size with operating conditions, but this was not accomplished because of the nature of the equipment and its semicontinuous method of operation. The crystal size distribution was not consistent from batch to batch. The crystal size generally began as a small size that grew larger and was eventually removed as product. Then a new batch of fine crystals was generated that in turn grew in size. A larger scale apparatus with some sort of crystal classification system, such as an elutriation leg, would give more meaningful results on the crystal size distribution. High NaOH concentrations generally resulted in more small crystals than did the lower NaOH concentrations. It was demonstrated on this small-scale equipment that NaOH-free crystals of moderate particle size can be produced from these solutions by vacuum evaporative crystallization. More refined operating conditions will have to be evaluated in larger scale, continuous equipment that more closely simulates commercial-scale equipment.

Actual Leach Solution

Four crystallization tests were performed with a solution produced from leaching a chromite fusion product rather than using synthetic solutions. Twenty-four kilograms of a fusion product produced from Eight Dollar Mountain laterite was leached with methanol in three separate stages at 30 pct solids to remove the bulk of the unreacted NaOH. A countercurrent leach could not be performed because of insufficient material and time left in the testing program. The residue from the methanol leach was given a single aqueous leach at 35 pct solids to produce solution for crystallization. The solution concentration using 35 pct solids is approximately equal to that which would be obtained in a countercurrent leach at 30 pct solids. This solution, containing 46 g/L NaOH, 212 g/L Na_2CrO_4, 17.6 g/L Al, and 0.24 g/L Si, then was treated with waterglass to remove the aluminum impurity. The solution, after treatment, contained 0.11 g/L Al and 0.69 g/L Si. Because of the extended period of time the solution was exposed to air during the filtering operation after the aqueous leach and during the impurity removal procedure, the solution absorbed CO_2 from the air to produce 15 to 16 g/L Na_2CO_3. Attempts to remove this impurity by precipitation with lime met with limited success. Fifteen liters of a final solution containing 11 g/L Na_2CO_3, 49 g/L NaOH, and 253 g/L Na_2CrO_4 were available for crystallization studies.

A synthetic mother liquor with the composition of 700 g/L NaOH and 175 g/L Na_2CrO_4 was used in the crystallization tests. The crystallizer was operated at a vacuum of 27 in Hg, resulting in a boiling temperature of 90° C. A total of 11.6 L of feed solution was processed in the crystallizer, producing 2.84 kg of crystals. This represented a recovery of 96.6 pct of the Na_2CrO_4 fed to the system. The average size of the crystals was 42 mesh. The crystals contained less than 0.01 pct Al, Si, and NaOH, but the Na_2CO_3 content averaged 3.7 pct. In any future tests, care must be taken to minimize the time the aqueous solutions are exposed to air to avoid the problem of carbonate contamination. The Na_2CO_3 is the least soluble component and will contaminate the crystals if present.

SUMMARY AND CONCLUSIONS

Laboratory-scale testing showed that low-grade domestic chromite concentrates that are not suitable for chemical processing by present commercial methods can be treated successfully by a procedure devised by the Bureau of Mines. The procedure involves reacting the chromites with fused NaOH under oxidizing conditions to form Na_2CrO_4, which is then recovered by leaching and crystallization. Product crystals of Na_2CrO_4 were obtained that contained less than 0.01 pct NaOH and whose average particle size ranged from 28 to 65 mesh.

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